AGING OF COLD-MIX ASPHALT PAVEMENTS

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INTRODUCTION

One type of cold-mix asphalt is emulsified asphalt which is a mixture of unheated mineral aggregate with a dispersion of asphalt cement in water that contains a small amount of emulsifying agent. Emulsified asphalts offer the advantages of more favorable economics and less polluting operations which are more commonly used for medium and light-traffic than heavy traffic applications [1]. The focal point of our research on asphalt pavements is the emission of volatile organic compounds (VOC) from different cold-mix formulations [2]. It appears, however, that the emission (or retention) of volatiles is closely related to the aging of the cold-mix asphalt pavements. The objective of this study is to investigate the changes in the chemical composition of the emulsified asphalt pavements as a result of aging. We have analyzed the samples of pavements aged in-place on the roads from 9 months to 10 years by distillation, FTIR, GC, and GC/MS. Two different formulations of emulsified asphalts used in this study are a proprietary cold-mix (HGP) developed by Heilman Pavement Specialties, Inc, Freeport, PA and Pennsylvania State Department of Transportation standard cold-mix prepared with E-5 emulsion (FB-1).

EXPERIMENTAL

Along with the fresh asphalt samples, two, four, six, and ten year-old HGP pavements and , nine month and eight year-old FB-1 pavements were sampled from local roads exposed to similar climate and traffic load in Beaver and Armstrong counties in Pennsylvania. In laboratory, fresh samples of the two cold-mix asphalts were exposed to air under ambient conditions in a fumehood for fifty days.

Distillation tests were conducted on fresh and aged asphalt samples using a standard apparatus and procedure (AASHTO T 59-86, ASTM D-244-83 a) with some modifications [3]. A maximum temperature of 700°F was used in the distillation tests, collecting distillates also at lower temperatures (e.g., 350°F and 500°F). The distillates were analyzed in a Perkin-Elmer 8500 gas chromatograph with fused silica capillary column (30 m X 0.25 mm) coated with 50% methyl- and 50% phenylpolysiloxane (Rtx 50; Restek Co.) and in a Kratos MS-80 gas chromatograph / mass spectrometer.

FTIR analysis of the fresh and aged asphalt samples was carried out using a Digilab FTS-60 Infrared spectrometer. The samples were prepared as thin films on KBr windows from chloroform extracts obtained after soaking the asphalt samples in chloroform for 24 h . To obtain the FTIR spectra 64 scans were collected and averaged with a resolution of 2 cm^{-1}.

RESULTS AND DISCUSSION

The results from the GC and GC-MS analyses of the distillates from the fresh asphalts showed that the FB-1 distillates are dominated by normal and branched octane (C_8) and nonane (C_9) in

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addition to higher alkanes with carbon numbers C_{10} through C_{17} and traces of alkylbenzenes and alkylcyclohexanes. The distillates obtained from HGP, on the other hand, consist principally of long chain normal and branched alkanes with nine to sixteen carbon atoms (C_9 to C_{16}). In addition, alkylbenzenes and alkylnaphthalenes (C_7 to C_{13}) as well as alkylcyclohexanes and alkyltetralins (C_9 to C_{15}) are present at low concentrations. As summarized in the chromatograms shown in Figure 1, the hydrocarbon additives in FB-1 are much more volatile than those in HGP, considering that the same asphalt cement was used in both HGP and FB-1.

The high volatility of the hydrocarbons in FB-1 was also demonstrated upon exposing the fresh samples of the two asphalts to ambient conditions in a fume hood for 50 days. After 50 days all the distillable hydrocarbons from FB-1 was lost, while HGP retained a major fraction (30% by volume) of the distillable hydrocarbons. The gas chromatogram of the distillate obtained from the exposed HGP is shown in the chromatogram c in Figure 1. It is interesting to note that both low and high ends of the hydrocarbons are absent in the distillate obtained from this sample. The distillation of the aged pavements heated to a maximum temperature of 700°F showed that distillate yield first decreased (from 3.5 mL in fresh sample to 1 mL in 4 year-old) and then increased (to 1.3 mL in 6 year-old sample and to 2.7 mL in 10 year-old sample) with the further increase in age. Figure 2 shows the gas chromatograms of the distillates obtained from the fresh mix and 2, 4, 6, and 10 year-old HGP pavement samples. No data were obtained for the FB-1 samples since the aged FB-1 pavements did not yield any distillate. Similar to the 50-day exposed asphalt,the aged HGP samples show different hydrocarbon distributions from that of fresh HGP. It can be seen that as the age of the samples increases, the distribution of dominant hydrocarbons shifts gradually from the higher mass region (C16 to C20 for fresh and 2 year old samples) to lower mass region (C14 to C18 for the samples older than two years). The distribution of the unresolved complex mixture (UCM), extending from retention time 20 min to 50 min., shows the same trend as that of the identified hydrocarbons in the samples- a decreasing maximum with increasing age. The total intensities of the peaks for selected isoprenoids (C14, C15, C16-isoprenoids, pristane, and phytane) and the corresponding normal alkanes (n-C14, n-C15, n-C16, n-C19, and n-C20) were calculated by integration. It was found that the relative ratio of the selected isoprenoids to the corresponding normal alkanes increased gradually with the increasing age.

These changes in the chemical composition of hydrocarbons in the asphalt pavements with the increasing age can result from various processes such as evaporation, microbial degradation, oxidation, and thermal/catalytic cracking and polymerization reactions. Possible effects of these processes are discussed below in relation to the experimental data obtained in this study.

According to a commonly used definition, volatile organic compounds (VOC) are defined as the chemicals which has 0.002 psi vapor pressure at 0°C. According to this definition, almost all the distillable hydrocarbons found in FB-1 (C8 to C9) can be classified as VOC. It is not surprising to find that these hydrocarbons evaporated after exposure to air for 50 days. The evaporation of light hydrocarbons from the samples also indicates that the hydrocarbons were bound loosely in the asphalt. This is probably the reason why none of the distilled hydrocarbons was observed in the 9 month and 8 year-old FB-1 pavements. The evaporation of the lower molecular weight hydrocarbons (C9 to C12) in HGP also explains the loss of lighter ends in the aged samples, as shown in Figures 1 and 2. The retention of higher molecular weight hydrocarbons (over C13), in HGP asphalts over extended periods of time (up to 10 years) is, however, noteworthy, and indicates that the hydrocarbons are more strongly bonded in HGP and are not readily released to the atmosphere. Evaporation alone does not, however, explain all the changes observed with aging.

It is well known that aerobic or anaerobic microbial degradation plays an important role in petroleum alteration processes and that anaerobic degradation is much slower than aerobic decay[4] . A suggested order of vulnerability of hydrocarbons to microbial degradation follows[5]:

   n-alkanes > branched alkanes > low ring cyclic alkanes > aromatics > high ring cyclic alkanes.

A selective depletion of n-alkanes by microbial activity should result in decreasing the ratio of the concentration of n-alkanes to that of the isoprenoids. A gradual decrease in this ratio with age in the pavement samples suggests that anaerobic biodegradation may have contributed to the observed chemical changes. Microbial degradation does not, however, explain why the hydrocarbon distribution shifted from the higher mass (C16 to C20) to the lower mass region (C14 to C16) with the increasing age. Since the low molecular weight hydrocarbons is more readily consumed by the bacteria[4], a shift to a higher, not to a lower, mass region should be expected in the distribution of the hydrocarbons with the increasing age.

The results from the 50-day aging of the asphalt exposed to air combined with those obtained with the aged pavements strongly suggests that thermal/catalytic chemical reactions (oxidation, cracking, and polymerization) played a key role in producing the observed chemical changes. The shift in hydrocarbon distribution to lower mass regions in aged HGP pavements can be explained by cracking and/or polymerization of long paraffin chains. The dramatic change in the composition of distillable hydrocarbons obtained from the 50-day old sample, the complete removal of heavy ends in addition to light ends over a relatively short time period, can be explained by the polymerization of high molecular paraffins (in the presence of oxygen and light). For the aged pavement samples starting as compressed and sealed asphalts with limited access to oxygen and light, polymerization reactions should be expected to proceed much more slowly with thermal/catalytic cracking reactions becoming important over extended periods of time. It can be seen that the major change observed from the fresh to 4 year-old sample is the shift in the hydrocarbon distribution to lower masses, in addition to increasing ratio of isoprenoids to n-alkanes. This trend, combined with lower distillate yields obtained with 2 and 4 year-old samples, can be explained by polymerization of high molecular weight, but distillable alkanes to produce higher molecular weight nondistillable hydrocarbons. The increasing ratio of isoprenoids to n-alkanes can be attributed to higher reactivity of n-alkanes than that of isoprenoids in polymerization reactions and/or to bacterial degradation processes. The changes in going from 4-year to 10-year old sample are much less pronounced without a major shift in hydrocarbon distribution. The increasing distillate yield in going from the 4 year-old to 6 and 10 year-old pavements suggests that cracking reactions which produced distillable hydrocarbons were important in aging from 4 to 10 years period. The increasing concentrations of aromatic compounds with aging in this period also suggests that thermal/catalytic cracking reactions had taken place. Possible catalytic effects[6,7] of the aggregates used (limestone and blast furnace slag) and temperature increases within the pavement because of oxidation reactions are plausible conditions for thermal/catalytic cracking reactions which can occur over extended periods of time under the pavement conditions.

FTIR spectra obtained for the chloroform extracts of the fresh and aged samples FB-1 and HGP are shown in Figures 3. The spectra of the FB-1 fresh mix, 9 month- and 8 year- old pavement samples shown at the top of Figure 3 indicate that oxidation and cracking or aromatization reactions had taken place in the time period from 9 months to 8 years. The spectra of the fresh and 9-month old samples appear to be quite similar. The most notable change in the FTIR spectrum of the 8-year old sample is the appearance of a strong band in 1700 cm^{-1} region which is assigned to carbonyl groups, indicating the incorporation of oxygen into the asphalt pavement similar to the previous data obtained on different hot-mix asphalt samples[6,8,9]. Other distinct changes observed in the spectrum of the 8-year old are the stronger aromatic C-H stretch and out-of-plane bending bands at 3050 cm^{-1} and at 700-900 cm^{-1}, respectively, coupled with a decreased intensity of 2920 cm^{-1} peak relative to that of 2950 cm^{-1} peak. These changes can be attributed to cracking/aromatization reactions which would result in the shortening of paraffinic chains and removal of alkyl side chains from the aromatic rings. Instead of relatively strong absorption at 860 cm^{-1} seen in fresh and 9 month-old samples, assigned to isolated hydrogen, 8 year-old sample shows a more intense peak at 750 cm^{-1} which is assigned to four neighboring hydrogens on an aromatic ring. The shift from 860 cm^{-1} to 750 cm^{-1} indicates the formation of new aromatic rings and/or the removal of alkyl chains from the existing aromatic rings. The increasing intensity

of the aromatic carbon ring stretch band at 1600 cm^{-1} can be taken as a supporting evidence for the formation of new aromatic rings from alkanes.

FTIR spectra of the HGP series shown at the bottom of Figure 3 shows a more gradual change in composition than the FB-1 series, except for the broad bands observed at 3300-3600 and 1100 cm^{-1} region of the 10 year-old sample. These bands are tentatively assigned to water. Parallel to the behavior of the FB-1 samples, 9 month-old HGP sample has a very similar spectrum to that of the fresh asphalt. The 4 year-old sample shows the appearance of carbonyl band at 1700 cm^{-1} which becomes stronger in the 10 year-old sample. The relative intensity of this band however is much lower than that observed in the 8 year-old FB-1 pavement, indicating that the HGP pavement is more resistant to oxidation. Since no oxygenated compounds were observed in the distillates obtained from HGP samples, it can be inferred that only the high molecular weight constituents of the asphalt incorporate oxygen. As different from the trend observed for the FB-1 pavement, aromatic C-H stretch (3050 cm^{-1}) decreases with the decreasing out-of-plane bending at 860 cm^{-1} as a function of aging. In contrast to FB-1 8 year-old, there is no significant change in the intensity of the 750 cm^{-1} peak (four neighboring hydrogens on the aromatic rings) with the increasing age. These observations may be explained by the coupling of aromatic rings with other aromatic rings or aliphatic hydrocarbons during the aging of HGP as opposed to dealkylation or formation of new aromatic C-H functionalities in the aged FB-1 pavement. Another difference between the aging behavior of HGP and FB-1 is that in the period between 9 months and 10 years aliphatic functionalities in HGP do not show much change in structure.

The differences in the aging behavior of HGP and FB-1 pavements can be mostly attributed to the different abilities of these pavements in retaining the smaller molecular weight (distillable) hydrocarbons. The presence of these hydrocarbons at high concentrations in HGP pavements is believed to be responsible for their lower susceptibility to oxidation.

CONCLUSIONS

The aging behavior of the pavements from the two different emulsified asphalt mixes FB-1 and HGP are rather different in that FB-1 shows more extensive oxidation and thermal degradation whereas HGP is subjected to subsequent polymerization and cracking reactions during aging. These differences are believed to be due to the differences in the formulation of the two mixes, mainly to the ability of the HGP pavements to retain the distillable hydrocarbons.

ACKNOWLEDGEMENTS

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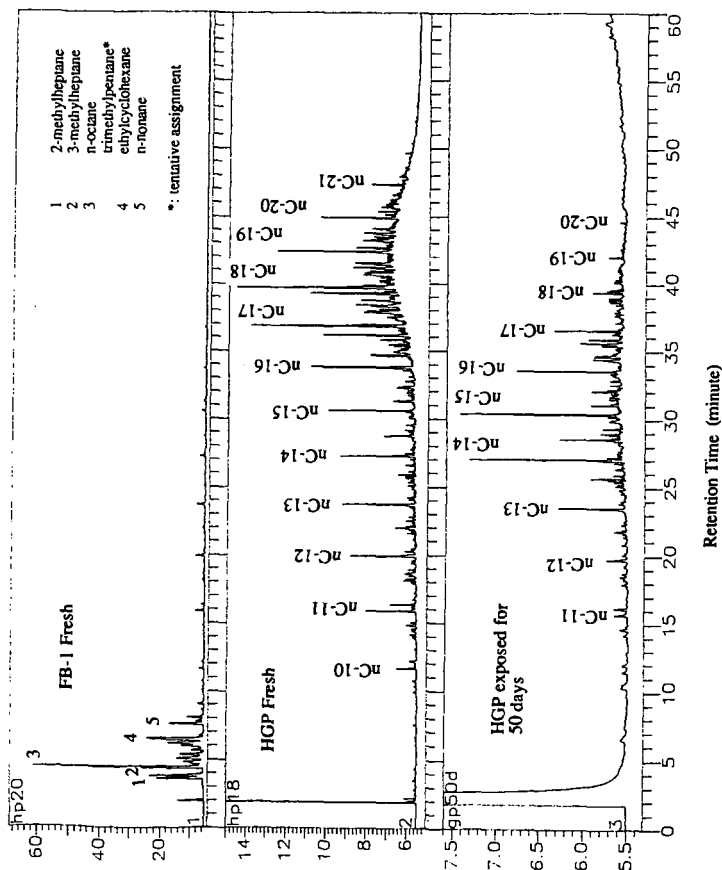9. Dorrence, S. M., Barbour, F. A., Petersen, C. J., Anal. Chem. 46, 2242, 1974.

Figure 1. Gas chromatograms of the distillates obtained from FB-1 fresh (top), HGP fresh (middle) and HGP exposed to air and light for 50 days in a fumehood.
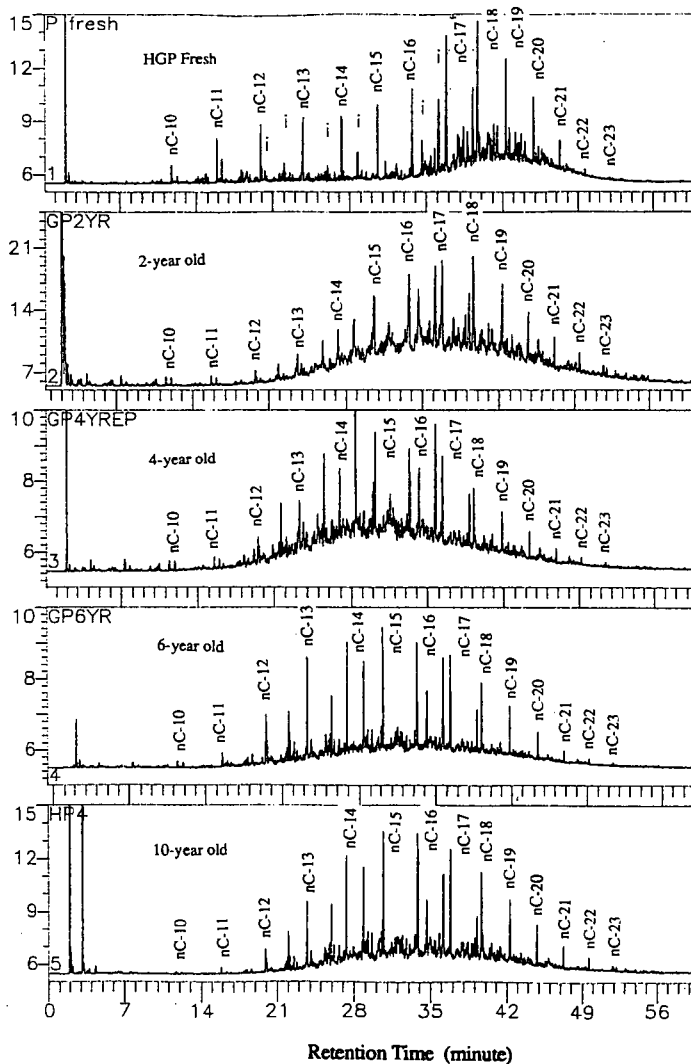
Figure 2. Gas Chromatograms of the distillates obtained from fresh HGP and 2, 4, 6, and 10 year-old pavement samples.
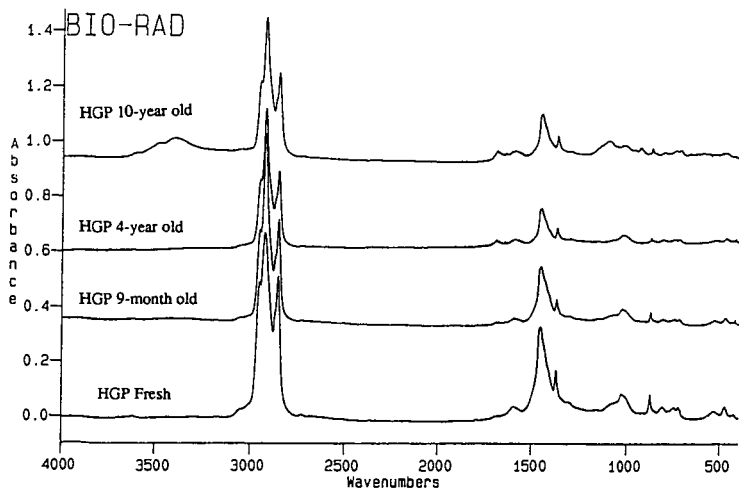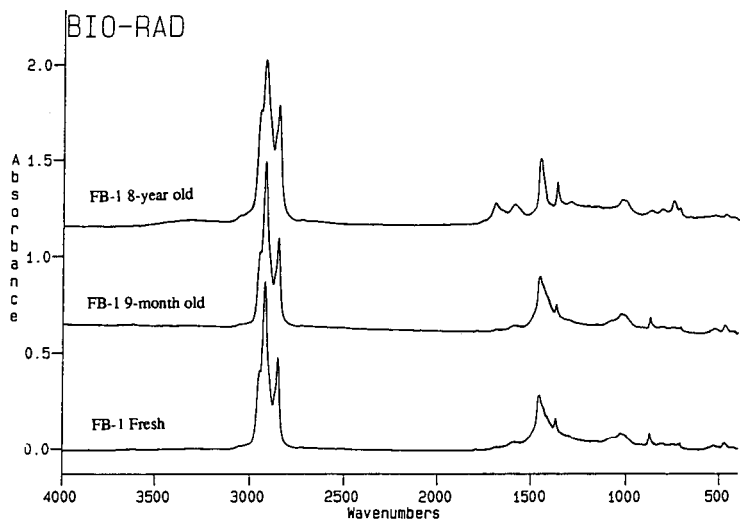
Figure 3. FTIR spectra of fresh and aged FB-1 and HGP pavements extracted with chloroform.